

Fluorination of Aluminium Complexes

Preparation of NHC Stabilized Al(III)fluorides: Fluorination of [(SIMes)AlMe₃] with SF₄ or Me₃SnFPooja Tomar,^[a] Thomas Braun,^{*,[a]} and Erhard Kemnitz^{*,[a]}

Abstract: Various reaction routes have been developed to synthesize the *N*-heterocyclic carbene (NHC) stabilized Al(III) fluorides [(SIMes)Al(F)₃] (**2**) and [(SIMes)Al(F)Me₂] (**3**) through fluorination of [(SIMes)AlMe₃] (**1**) (SIMes: 1,3-bis(2,4,6-trimethyl-

phenyl)-imidazolidin-2-ylidene) with fluorinating agents such as SF₄, SF₆ and Me₃SnF. The reactivity of **2** was investigated towards a F/Cl exchange reaction by treating it with Me₃SiCl.

Introduction

Aluminium trifluorides and derivatives have been used as heterogeneous Lewis acid catalysts to produce chlorofluorocarbons and hydrofluorocarbons.^[1] β-AlF₃ was shown to catalyze intermolecular Cl/F exchange reaction, for instance to convert the greenhouse gas trifluoromethane CHF₃ into CHCl₃.^[2] Nanoscopic, amorphous aluminium fluorides such as high-surface aluminium fluoride (HS-AlF₃) and aluminium chlorofluoride (ACF, AlCl_xF_{3-x}, x = 0.05–0.3) are known to exhibit a Lewis acidity comparable to that of SbF₅.^[1b] In the presence of silanes or germanes they are useful compounds to mediate hydrodefluorination or dehydrofluorination reactions of fluorinated alkanes.^[3] Nanoscopic aluminium fluorides can be synthesized by treating alumina or AlCl₃ with chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), or with HF sources. Case and Nyman also documented in 1962 the decomposition of SF₆ at AlCl₃ at 180–200 °C to give within 24 h AlF₃ along with sulfur chlorides.^[4] SF₄ was also used as fluorinating agent to obtain AlF₃ by reaction with aluminium hydroxide [Al(OH)₃] at 20 °C.^[5]

There are rare examples reported for the synthesis of molecular AlF₃ complexes bearing neutral ligands. Notably, Reid et al. documented a 1,4,7-triazacyclononane (tacn) stabilized AlF₃ complex solvated with water molecules.^[6] Kolis and co-workers described the hydrothermal synthesis of AlF₃(NH₃)₂ by treating

AlN and NH₄F at 400 °C in supercritical ammonia.^[7] In 1957 Ziegler reported on the generation of the first organoaluminium fluorides.^[8] The organyl groups make the compounds soluble in various organic solvents, and hence, reactivity in solution can be investigated. The properties of organoaluminium fluorides and their applications have been covered very extensively in reviews by Roesky.^[9] Organoaluminium fluorides such as dimethylaluminium fluoride (Me₂AlF)₄ were established to access aluminium fluoride clusters by Roesky and co-workers.^[10] Kemnitz et al. also showed that reactions of Al(OiPr)₃ with HF in pyridine as a solvent yield polynuclear aluminium alkoxide fluoride compounds.^[11] In a recent report Crimmin and co-workers reported on the activation of C–F bonds of fluoroalkenes by treating them with an Al(I) complex to give organoaluminium fluorides such as [HC(CMeNAr)₂]Al(F)₂ (Ar = 2,6-*i*Pr₂C₆H₃).^[12]

N-heterocyclic carbenes NHCs are widely used as ligands for stabilizing a wide range of group 13 compounds resulting in complexes bearing unique and interesting properties.^[13] Lewis pairs with Al-based Lewis acids have been prepared for instance by treatment of AlMe₃ with aromatic NHCs.^[14] Here we present, the development of reaction routes to access NHC stabilized aluminium fluorides by fluorination of [(SIMes)AlMe₃] (**1**) (SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene). Suitable fluorinating agents are SF₄, SF₆ and Me₃SnF.

Results and Discussion

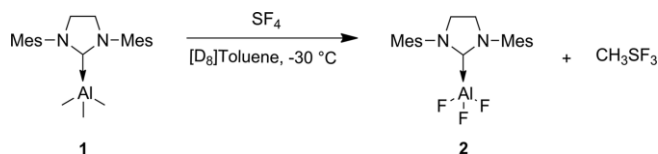
Treatment of complex [(SIMes)AlMe₃] (**1**) with SF₄ in toluene yielded the aluminium trifluorido complex [(SIMes)Al(F)₃] (**2**). The reaction was monitored by NMR spectroscopy and at –30 °C a complete fluorination as well as the generation of considerable amounts of CH₃SF₃ were observed (Scheme 1). In the ¹⁹F NMR spectrum a broad resonance at δ = –164.5 ppm was found for **2** (Figure 1). This resonance is consistent with data for four-fold coordinated aluminium fluorides such as the complex [HC(CMeNAr)₂]Al(F)₂ (Ar = 2,6-*i*Pr₂C₆H₃).^[12] A signal at δ = 49.8 ppm in the ²⁷Al NMR spectrum appears also in a typical

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range for fourfold coordinated aluminium halide species.^[15] The ^{19}F NMR spectrum shows two signals for CH_3SF_3 at $\delta = -50.6$ ppm and 60.9 ppm, which are in accordance to the literature.^[16]



Scheme 1. Formation of SIMes aluminium(III)fluoride **2**.

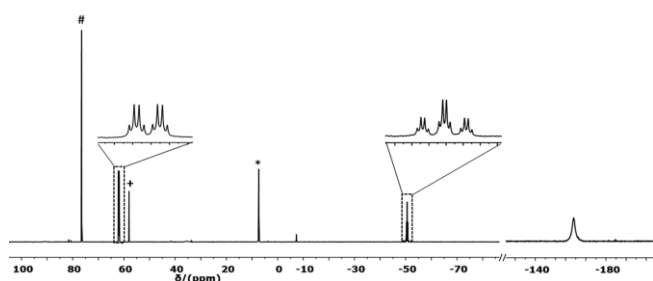
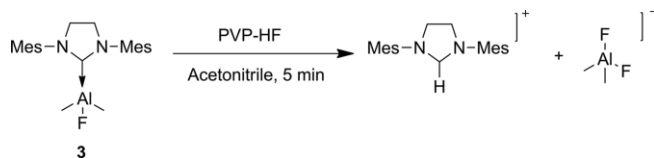


Figure 1. ^{19}F NMR (282.4 MHz, $[\text{D}_8]\text{toluene}$, $-30\text{ }^\circ\text{C}$) spectrum showing signals for the formation of complex **2** and CH_3SF_3 . $^{\#}\text{SO}_2$ (impurity from SF_6), $+\text{SF}_6$, $^{\circ}\text{CH}_3\text{SOF}$.

The reactivity of **1** towards SF_6 has also been investigated. In general SF_6 activation has been considered to be challenging, but several interesting procedures were developed in the past years.^[17] When the aluminium complex $[(\text{SIMes})\text{AlMe}_3]$ (**1**) was treated with SF_6 and the reaction mixture was heated at $70\text{ }^\circ\text{C}$ for 15 h, monofluorination at aluminium took place to give a complex in low yield (30 %), the data of which are consistent with $[(\text{SIMes})\text{Al}(\text{F})\text{Me}_2]$ (**3**). The reaction did not proceed further, even after prolonged reaction times. When complex **1** and SF_6 were treated together at 311 nm under UV light for 24 h, the formation of **3** and subsequently of the aluminium trifluoride complex **2** was observed. In the ^{19}F NMR spectrum of **3** a broad signal was found at $\delta = -169.9$ ppm. The ^1H NMR reveals a doublet at $\delta = -1.09$ ppm with a coupling constant of $^3J_{\text{H-F}} = 3.2$ Hz for the methyl groups attached to the Al center. The coupling constant is in the expected range of $^3J_{\text{H-F}}$ values reported for organofluoroaluminates.^[18]

Along with complex **3** the evolution of methane was also observed as indicated by ^1H NMR spectroscopy. This suggests the presence of HF in the reaction mixture, which might react with **1** to yield CH_4 . When the activation of SF_6 was performed in the presence of CsF , no reaction was observed, presumably due to trapping of HF by the base, which further supports a fluorination of **1** by HF. However, treatment of complex **3** with PVP·HF as an HF source gave the protonated SIMes and $[\text{AlF}_2\text{Me}_2]^-$,^[19] whereas a reaction of **1** with PVP·HF also generates the protonated carbene and $[\text{AlF}_4]^-$ (Scheme 2). The same products were formed when the reaction mixture of **1** and **3** were kept for 2 days at room temperature.

Note that it was reported in the literature that SIMes and SF_6 can react at $80\text{ }^\circ\text{C}$ within 48 h to give a 2,2-difluoroimidazolidine

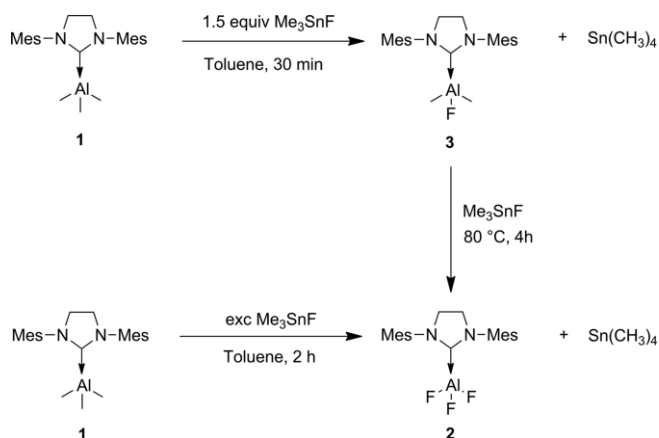


Scheme 2. Addition of HF to complex **3**.

derivative in very low yield.^[17d] The reaction can be promoted by photolysis. 2,2-Difluoroimidazolidine $\text{C}_3\text{H}_4\text{N}_2(\text{Mes})_2\text{F}_2$ is water sensitive and can react to furnish HF and the corresponding urea derivative. Therefore, it can be speculated that when complex **1** was treated with SF_6 at $70\text{ }^\circ\text{C}$ some decomposition occurs to yield SIMes, which then activates SF_6 to produce 2,2-difluoroimidazolidine and the respective 2-thiocarbene. The former reacts with adventitious water to yield HF which fluorinates **1**. Note, that on adding complex **1** to the 2,2-difluoroimidazolidine the generation of complex **3** was observed with very low conversion.

To develop a more reliable synthesis of the fluorido compounds **2** and **3**, Me_3SnF was employed as fluorination agent. Note that Me_3SnF has been used as fluorinating agent for fluorination of transition and main group chlorides.^[9,20] Me_3SnF was also reported to convert dimethyl alan or aluminium hydrides into aluminium fluorides as shown for the synthesis of aminoalane difluoride $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Al}(\text{F})_2]$ and diamidoaluminium fluoride $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2(\text{CH}_2)_3\text{AlF}(\text{NMe}_3)$.^[21]

Reaction of complex **1** with 1.5 equivalents of Me_3SnF led to the generation of **3** with full conversion of complex **1**. Tetramethyltin was also formed and identified in ^1H NMR spectrum by a signal at $\delta = 0.05$ ppm, in ^{13}C NMR spectrum at $\delta = -9.4$ ppm and in ^{119}Sn NMR spectrum at $\delta = 0.00$ ppm.^[22] When three equivalents of Me_3SnF were added to complex **1** a mixture of complexes **2** and **3** was observed after 2 h (ratio: 0.5:1). Monitoring the reaction by NMR spectroscopy revealed that **3** converted into **2** when heated at $80\text{ }^\circ\text{C}$ for 4 h in the presence of Me_3SnF . However, treatment of complex **1** with an excess of Me_3SnF for 2 h gave complex **2**, as evidenced by the resonance at -164.8 ppm in the ^{19}F NMR spectrum (Scheme 3, Figure 2).



Scheme 3. Fluorination of complex **1** with Me_3SnF .

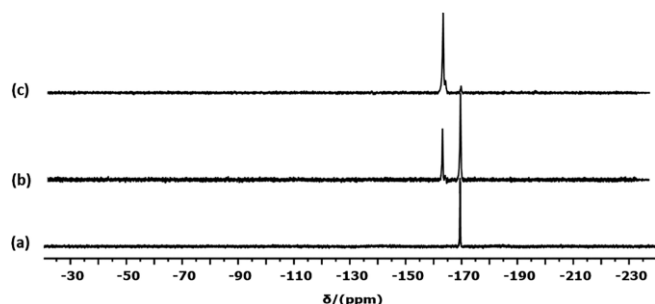
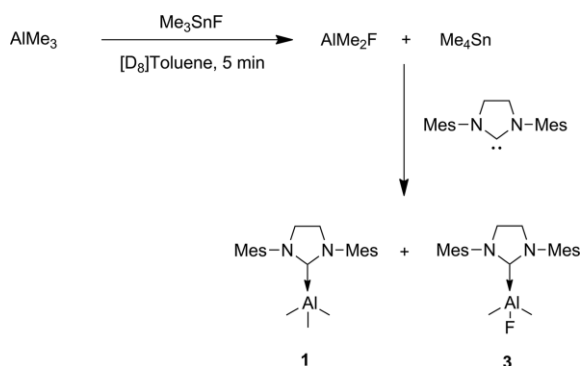


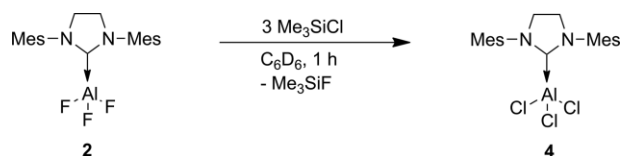
Figure 2. ^{19}F NMR spectra of the reaction of **1** with Me_3SnF (3 equiv.); (a) after 30 min, (b) after 2 h, (c) after heating the mixture of complex **2** (-164.8 ppm) and complex **3** (-169.9 ppm) at 80°C for 4 h.

For comparison, AlMe_3 was also treated with Me_3SnF and the generation of AlMe_2F was observed (Scheme 4). The latter exists as a dynamic mixture of dimers, as described in the literature.^[23] The measured $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum shows resonances at $\delta = -0.43$ ppm, -0.55 ppm, -0.63 ppm and -0.69 ppm, but not with equal intensities as described in the literature.^[24] It can be speculated that binuclear Al compounds bearing only one fluorine atom $\text{Al}_2\text{Me}_5\text{F}$ were also present. However, the ^{19}F NMR spectrum reveals four resonances at $\delta = -143.6$ ppm, -145.8 ppm, -148.9 ppm and -150.8 ppm. These values are in accordance with data reported by Oliva et al.^[25] Upon addition of SIMes to the reaction mixture the generation of complexes **1** and **3** was observed (Scheme 4), which supports the proposed structure of complex **3**. There is no hint for the generation of $[(\text{SIMes})\text{Al}(\text{F})_2\text{Me}]$.



Scheme 4. Formation of complex **3** using Me_3SnF as fluorinating reagent.

It has been shown that metal fluoro complexes can be converted into chlorido complexes using chlorosilanes.^[26] Indeed, when Me_3SiCl was added to the SIMes stabilized aluminium(III)fluorido complex $[(\text{SIMes})\text{Al}(\text{F})_3]$ (**2**) the chlorido complex $[(\text{SIMes})\text{Al}(\text{Cl})_3]$ (**4**) was obtained along with Me_3SiF (Scheme 5). This conversion further confirms the identity of complex **2**. A signal at $\delta = 104.7$ ppm was found in the ^{27}Al NMR spectrum,



Scheme 5. Transformation of **2** into **4** with Me_3SiCl .

which is consistent with data for **4**, synthesized independently.^[27] Signals for Me_3SiF were observed at $\delta = -156.9$ ppm in $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum and at $\delta = 30.3$ ppm in ^{29}Si NMR spectrum.^[28]

Conclusions

Herein we have explored different synthetic routes to access NHC stabilized aluminium(III)fluorido complexes. $[(\text{SIMes})\text{Al}(\text{F})_3]$ (**2**) was formed when $[(\text{SIMes})\text{AlMe}_3]$ (**1**) was treated with SF_4 , whereas a reaction with SF_6 yielded $[(\text{SIMes})\text{Al}(\text{F})\text{Me}_2]$ (**3**). Me_3SnF was also employed for fluorination of complex **1** to develop an alternative more reliable way to synthesize **2** and **3**. Complex **1** can be converted into the respective chlorido complex **4** via F/Cl exchange reaction by reaction with Me_3SiCl .

Experimental Section

Instruments and Methods: All reactions were carried out in a glove box under argon atmosphere or using standard Schlenk techniques under inert conditions. The reaction with SF_4 was performed on a stainless steel vacuum line. Solvents were distilled using conventional methods and degassed prior to use. Other reagents were bought either from Sigma-Aldrich or abcr. The NMR spectra were recorded at 25°C , if not stated otherwise, on a Bruker DPX 300, a Bruker Avance III 300, or a Bruker Avance II 500 spectrometer. The ^1H NMR spectra were referenced to residual $[\text{D}_7]\text{Toluene}$ at $\delta = 7.09$ ppm or $\text{C}_6\text{D}_5\text{H}$ at $\delta = 7.16$. The ^{19}F NMR spectra were referenced to external CFCl_3 at $\delta = 0.0$ ppm. The ^{29}Si NMR spectrum was referenced externally to TMS at $\delta = 0.0$ ppm. $^{27}\text{Al}\{^1\text{H}\}$ NMR spectra were referenced externally to AlCl_3 in D_2O at $\delta = 0.00$ ppm. 1,2-Difluorobenzene at $\delta = -138.1$ ppm in the ^{19}F NMR spectrum was used as an external standard for quantification.

1,3-Bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene (SIMes) was synthesized by following the procedure described in the literature.^[29] The NHC stabilized aluminium complex **1** was synthesised by treating saturated imidazolidine mesityl carbene (SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene) with AlMe_3 (2 M in Toluene) as reported.^[14] Trimethyltin fluoride (Me_3SnF) was synthesized by treating trimethyltin chloride (Me_3SnCl) with potassium fluoride (KF) in a water/ethanol mixture.^[30]

Caution! SF_4 is a toxic and corrosive gas which easily hydrolyses to give HF and exposure to these chemicals can cause serious injuries.

Formation of Complex $[(\text{SIMes})\text{Al}(\text{F})_3]$ (**2**)

Method A: Fluorination with SF_4 : In a PFA tube complex $[(\text{SIMes})\text{Al}(\text{Me})_3]$ (**1**) (37.8 mg, 0.10 mmol) was dissolved in $[\text{D}_8]\text{Toluene}$ (0.3 mL). The solution was degassed by freeze-thaw cycles followed by condensation of SF_4 (1 equivalent) into it. The PFA tube was sealed and inserted into a NMR tube. The reaction mixture was then brought to -30°C and analysed by NMR spectroscopy.

Method B: Fluorination with Me_3SnF : In a Schlenk tube complex $[(\text{SIMes})\text{Al}(\text{Me})_3]$ (**1**) (37.8 mg, 0.10 mmol) was dissolved in toluene (5 mL) and an excess of Me_3SnF (6 equivalents) was added. The solution was stirred for 2 h at room temperature followed by filtration. The filtrate was evaporated in vacuo to obtain complex **2**. Yield: 68 %.

Spectroscopic Data for Complex **2:** ^1H NMR (300.1 MHz, C_6D_6): $\delta = 6.60$ (s, 4H, *m*-ArH), 4.24 (s, 4H, CH_2), 2.22 (s, 12H, *o*- CH_3), 2.01

(s, 6H, *p*-CH₃) ppm; ¹⁹F NMR (282.4 MHz, C₆D₆): δ = −164.5 (bs, AlF) ppm; ²⁷Al NMR (130.3 MHz, C₆D₆): 49.8 ppm.

Spectroscopic Data for CH₃SF₃:^[16] ¹H NMR (300.1 MHz, [D₈]Toluene, −30 °C): 4.96 (bs, CH₃SF₃) ppm; ¹⁹F NMR (282.4 MHz, [D₈]Toluene): δ = 62.1 (dq, 2F, ²J_{FF} = 73 Hz, ³J_{HF} = 15.3 Hz, CH₃SF₃), −50.6 (1F, tq, ²J_{FF} = 73 Hz, ³J_{HF} = 15.3 Hz, CH₃SF₃) ppm.

Formation of Complex [(SiMes)Al(F)Me₂] (3)

Method A: Fluorination with SF₆: In a PFA tube complex [(SiMes)Al(Me)₃] (1) (37.8 mg, 0.10 mmol) was dissolved in [D₈]Toluene (0.3 mL). The solution was degassed by freeze-thaw cycles followed by condensation of SF₆ (1 equivalent) into it. The PFA tube was sealed and inserted into a NMR tube. The reaction mixture was warmed up to room temperature and heated at 70 °C for 48 h to obtain complex 3. The yield after 48 h was found to be 30 % when calculated by using a capillary with 1,2 difluorobenzene (0.2 m in C₆D₆) as an external standard.

Method B: Fluorination with Me₃SnF: In a Schlenk tube complex [(SiMes)Al(Me)₃] (1) (37.8 mg, 0.10 mmol) and Me₃SnF (18.6 mg, 0.10 mmol) were dissolved in toluene (5 mL). The solution was stirred for 30 min at room temperature and filtered. The filtrate was then evaporated in vacuo to obtain complex 3. Yield: 62 %.

Spectroscopic Data for Complex 3: ¹H NMR (300.1 MHz, C₆D₆): δ = 6.59 (s, 4H, *m*-ArH), 3.04 (s, 4H, CH₃), 2.22 (s, 12H, *o*-CH₃), 2.06 (s, 6H, *p*-CH₃), −1.16 (d, 6H, ³J_{HF} = 3.07 Hz, AlCH₃) ppm; ¹⁹F NMR (282.4 MHz, C₆D₆): δ = −169.9 (bs, AlF) ppm.

Reactivity of Complex 2 towards Me₃SiCl: In a PFA tube complex [(SiMes)Al(F)₃] (2) (39.2 mg, 0.10 mmol) was dissolved in C₆D₆ (0.3 mL) and Me₃SiCl (3 equivalents) was added at room temperature. Formation of complex [(SiMes)Al(Cl)₃] (4) and trifluoromethylsilane (Me₃SiF) was observed after 1 h. The analytical data for complex 4 are in accordance with those in the literature.^[27]

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Keywords: N-heterocyclic carbenes · Aluminium fluorides · Sulfur fluorides · Tin fluorides

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